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LEACHING FROM BIOMASS COMBUSTION ASH

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SUMMARY: The use of biomass combustion ashes for fertilizing and liming purposes has been widely addressed in scientific literature. Nevertheless, the content of potentially toxic compounds raises concerns for a possible contamination of the soil. During this study five ash samples generated at four different Danish incineration plants were collected and analyzed for their chemical composition and leaching behavior. Batch leaching tests at Liquid-to-Solid ratio 2 l/kg were carried out. Although high total contents of nutrients (i.e. K and P) were detected, only K showed to be easily dissolvable in water. The content of the selected heavy metals (i.e. Cr, Ni, Pb and Cd) complied with the Danish Statutory Order on the use of bio-ash for agricultural purposes; however, critical releases of Cr were detected in the leachate extracts, especially in the fly ash. High alkaline pHs were measured in all eluates.

1. INTRODUCTION

Greenhouse gas emissions can be reduced by the substitution of biomass for fossil fuels in energy production. Accordingly and in agreement with the current European trends to use energy from renewable sources (Directive 2009/28/EC), biomass is becoming an increasingly popular source of renewable energy. During combustion, the biomass carbon content is released to the atmosphere but taken again up by the growing of new plants. From a global warming perspective, as long as the released carbon is sequestered by new biomass in forestry, then this process can be considered environmentally sustainable. In Denmark the consumption of wood chips for the production of primary energy has increased significantly from 2000 to 2012, approximately by four times (Energi Styrelsen, 2012). During incineration, solid by-products (i.e. ashes) are generated; increasing amounts of ashes have therefore been produced in the last decade. According to estimates, the combustion of wood generates about 2% by weight of ashes (James et al., 2012). Although their recirculation onto land for fertilizing and liming purposes have been widely proposed in literature, these ashes are commonly landfilled (Knapp & Insam, 2011). While this practice remove nutrients from the forest, landfilling also generate considerable costs for the incineration plants.

Biomass combustion ashes are rich in valuable nutrients (e.g. P, K, Ca and Mg) which if reused on field could sustain the soil fertility (e.g. Ingerslev et al., 2011). Similarly, because of their high alkalinity the residues could be suitable for liming purposes, contributing to increase pH of acidified soils. Nevertheless, their potential content of heavy metals and organic pollutants (e.g. Li et al.,

2012; Poster et al., 2006) may also bring forward concerns for environmental contamination of the soils. Depending on the input biomass type, combustion technology, operating parameters and final treatments, the ash residues can differ considerably in terms of both chemical and physical properties (Demeyer, Voundi Nkana, & Verloo, 2001). Consequently, the availability of the nutrients as well as heavy metals generally differs between individual ash products. Leaching tests can provide further information about release of ash constituents and their potential for contamination. Although biomass ashes have been widely studied for their chemical compositions (e.g. Vassilev et al., 2013), the geochemical mechanisms governing the leaching process need to be further addressed.

The aim of this paper is to study the composition and leachability of five different biomass ashes collected at four different Danish incineration facilities. The paper presents preliminary results as the research is still ongoing.

1. MATERIALS AND METHODS

Ash residues from four biomass combustion facilities were sampled late January 2014. Five samples of approximately 0.5-1 kg were collected from four incineration plants differently located in Denmark: Trustrup, Kjellerup, Ebeltoft, Herning. Two bottom ashes, one fly ash and two mixed ashes were considered. The collected materials were stored in hermetically closed plastic buckets and far from heat and light sources.

The ashes were analysed for both chemical composition and leaching behaviour. To obtain representative subsamples, the ashes were mixed and split with a riffle splitter. The sample's moisture content was measured according to EN 1097-5:2008 using approximately 80g of material. These dried samples were then crushed by means of a vibratory disc mill (agate discs) and non-crushable items (i.e. nails or unburned wood) were removed. A 0.25 g powder subsample was used for chemical characterization; here the material was digested by microwave assisted digestion (Multiwave Anton Paar 3000) according to EN 13656:2003: 2ml of HF, 6ml of HNO₃, 2 ml of HCl, 12ml of H₃BO₃ were used; to support the oxidation of the organic matter 2ml of H₂O₂ were also added. The digested samples were analysed by ICP-MS (7700x, Agilent Technologies) for their contents of Cr, Ni, Pb, Cd, P and K. A certified reference material (fly ash - BCR-176R) was also digested and analysed as previously described to test the reliability of both digestion and measurements. Duplicates were used.

The total organic carbon (TOC) contents were measured using 0.20 g of powdered ash by means of a Carbon/Sulfur analyzer (LECO induction furnace CS-200) according to the European standard procedure EN 13137:2001. The total carbon (TC) content was analysed by CHNOS Elemental Analyzer (vario MACRO cube) using 0.2 g of powdered ashes.

Batch compliance leaching tests at Liquid-to-Solid (L/S) ratio of 2 l/kg were carried out following the EN 12457-1:2002 standard procedure. Samples of 175g dry matter were put in 500ml polypropylene bottles and a final L/S ratio of 2 l/kg was established by adding distilled water. An end-over-end tumbler was used to ensure continuous mixing during the 24 hours. The leachate extracts were filtered through a 0.45 PTFE hydrophilic filter and divided in two subsamples: one was acidified by adding HNO₃ and analysed for its content of Cr, Ni, Pb, Cd, P and K by means of ICP-MS; the non-acidified subsample was used to determine the concentrations of total (TC) and non-volatile organic carbon (DOC) by carbon analyser (Shimadzu 5000A).

2. RESULTS AND DISCUSSION

Table 1 shows the measured contents of P, K, Cr, Ni, Cd and Pb, averaged according to the ash type: mixed, fly and bottom. The results of a recent Danish study (Ingerslev et al., 2011) and average composition data from bottom and fly ashes (ECN, 2014) are also here presented for comparison. Even though the ash composition is extremely variable, our measurements are generally in agreement with previous literature and also comply, to the extent of the analysed parameters, with the limits of the current Danish Statutory Order on the use of bio-ash for agricultural purposes (N. 818:2008). Higher contents of heavy metals were detected for the fly ash fraction. In contrast to typical literature trends (e.g. Pöykiö et al., 2007; Dahl et al., 2009; Pöykiö et al., 2012; Ingerslev et al., 2011), Pb was approximately two times higher in the bottom than in the fly ash samples. Although significantly lower contents of Cr were measured compared to Ingerslev et al. (2011), high variability in the Cr contents has been registered in literature with respect to different combustion technologies and input biomass (e.g. Supancic et al., 2014; ECN 2014). High contents of P and K were shown by all ash types confirming their potential reuse for fertilizing purposes.

The moisture content of the five samples substantially differed from each other, ranging between 8.1% and 54%. Low efficiency of the combustion process was noticed; high contents of unburned carbon were found in both fly ashes and mixed ashes: a TOC content of 17% was registered for the fly ash sample, followed by the mixed (7.4%) and finally the bottom ash samples (0.7%) (see Figure 1). A similar trend was shown by the TC, but with slightly higher values. The results are averaged by ash type.

The leachate extracts pHs were all found to be strongly alkaline, ranging between 13.0 and 13.9. Although a more quantitative characterization of the leachate buffer capacity (e.g. acid neutralization capacity) is needed, the high natural pH seems to confirm the suitability of the ash for liming purposes. However the solubility of the ash needs to be further addressed in order to avoid potential risks of pH shock in the soil ground water (Mahmoudkhani et al., 2007).

Table 2 presents the leachates analyses results from EN 12457-1:2002 averaged by ash type in comparison with regulatory limits. The measurements are also compared with a recent Danish study (Allegrini et al., 2011) addressing the leaching behaviour of biomass gasification bottom ashes. With regards to our samples, slightly higher concentrations of heavy metals (i.e. Cr, Ni and Pb) were detected in the fly ash eluate. Accordingly, while the eluate extracts from mixed and bottom ashes had concentrations similar to Allegrini et al. (2011), the ones from fly ashes were slightly higher. Cd was found below the limit of detection in all samples.

Despite high total K and P contents were detected, their leachability substantially differed to each other: K was measured at concentrations in the order of g/l whereas P was measured in mg/l. Likely K forms highly soluble minerals in the ash matrix, whereas P is more strongly bound into the ash matrix. With the only exception of the fly ash eluate, the concentration of P was found to be below the actual detection limit for both mixed and bottom ash eluates. This may suggest that the availability of P for plant uptake is extremely low.

Although most of the heavy metals were detected far below the acceptance criteria of landfills for inert material (2003/33/EC), the Cr concentrations were problematic: the fly ash eluate showed a concentration above the limit for not-hazardous landfills; similarly, the concentrations of bottom and mixed ashes eluates were above the acceptance limits of landfill for inert waste.

The total and dissolved organic carbon didn't show any clear pattern across the samples; instead, they were highly variable: average contents of 305 mg/kg ($\pm 32\%$) and 49 mg/kg ($\pm 40\%$) were found for TC and DOC, respectively. The influence of these parameters needs to be further investigated in relation to the leaching of heavy metals and possible complexation reactions which could enhance this process (see Van Zomeren & Comans, 2009).

Table 1: Elemental composition of the ash samples, averaged by type: mixed, fly and bottom ashes. Data from Ingerslev et al., 2011, ECN, 2014, and BEK 818/2008 are presented for comparison.

	Ingerslev et al, 2011										ECN, 2014				BEK 818/2008
	MIXED ASH	FLY ASH	BOTTOM ASH	Fly ash	Bottom ash	Wood Fly Ash		Wood Bottom Ash							
	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{50°C}	mg/kg _{50°C}	mg/kg _{dw}	n	mg/kg _{dw}	n						
P	14700	20100	9380	16800	22300	11500 (2900÷21100)		61	5400 (1100÷27000)		33	-			
K	57400	40000	44200	43500	70000	59300 (10600÷240000)		62	44100 (18000÷86200)		33	-			
Cr	44.4	62.7	38.3	159	505	109 (12.0÷464)		63	63.9 (15.0÷360)		47	100			
Ni	40.1	52.5	31.6	18.8	32.3	48.3 (11.0÷122)		63	23.3 (3.20÷65.0)		46	60			
Cd	5.19	15.7	0.312	14.6	n.d.	14.8 (1.60÷75.0)		61	1.80 (0.10÷15.0)		30	20			
Pb	13.9	22.2	48.2	19.3	3.93	174 (10.0÷709)		63	24.4 (6.20÷116)		46	250			

[dw: dry weight; kg_{50°C}: dry weight at 50°C; -: not stated; n.d.: not detected; n: number of samples; the numbers in the brackets refer to the minimum and maximum measured concentrations]

Table 2: Leachates analyses results from EN 12457-1 averaged by ash type (mixed, fly and bottom) in comparison with regulatory limits (2003/33/EC) and literature data (Allegrini et al., 2011).

L/S: 2l/kg	MIXED ASH	FLY ASH	BOTTOM ASH	Allegrini et al, 2011		2003/33/CE	
				Bottom ash	Inert	Not-hazardous	Hazardous
	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}	mg/kg _{dw}
P	<0.59	2.7	<0.59	0.021	-	-	-
K	23000	140000	5400	48000	-	-	-
Cr	3.5	9.8	2.2	2.2	0.2	4	25
Ni	0.052	0.22	0.067	0.013	0.2	5	20
Cd	<0.0014	<0.0014	<0.0014	<0.0002	0.03	0.6	3
Pb	0.0027*	0.012	0.0080*	0.0028	0.2	5	25

[*: one of the two samples had a concentration below the detection limit; the presented value is the average between the other sample concentration and the actual detection limit; dw: dry weight; -: not stated]

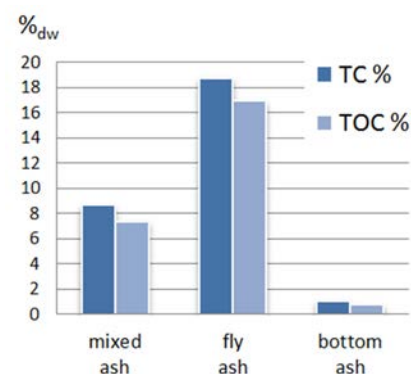


Figure 1: TC and TOC contents of the ash samples averaged by type. [dw: dry weight]

3. CONCLUSIONS

With respect to the analysed parameters, the selected ashes complied with the current Danish Statutory Order on the use of bio-ash for agricultural purposes (N. 818:2008). The share of available nutrients needs to be considered carefully if the purpose of the ash spreading is fertilization. Even though high total contents for both K and P were detected, only K showed to be easily dissolvable in water; moreover, ash residues generally lack of nitrogen which typically volatilizes during biomass combustion. Strongly alkaline pH values were measured for all leachate extracts; the use of ashes for liming purposes seems to be appropriate although the quantification of the ash buffer capacity is needful to confirm the feasibility of this practice. Even though the Cr total content complied with the limits for ash reutilization, its release when in contact with water was critical. More detailed studies aiming to identify the geochemical processes that govern the leaching release of heavy metals and nutrients are necessary. The influence of key parameters such as pH, dissolved organic matter and L/S ratios will be addressed within the study.

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